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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08J 7/04, C09D 133/16</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/36951</b> <b>(43) International Publication Date:</b> 9 October 1997 (09.10.97)
<b>(21) International Application Number:</b> PCT/US97/00512 <b>(22) International Filing Date:</b> 14 January 1997 (14.01.97)  <b>(30) Priority Data:</b> 08/626,409                      2 April 1996 (02.04.96)                      US  <b>(71) Applicant:</b> W.L. GORE & ASSOCIATES, INC. [US/US]; 551 Paper Mill Road, P.O. Box 9206, Newark, DE 19714 (US). <b>(72) Inventor:</b> SHEN, Ya, Xi; 232 Barberry Drive, Wilmington, DE 19808 (US). <b>(74) Agents:</b> CAMPBELL, John, S. et al.; W.L. Gore & Associates, 551 Paper Mill Road, P.O. Box 9206, Newark, DE 19714-9206 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> WATER AND OIL REPELLENT POLYURETHANE FILM  <b>(57) Abstract</b>  A hydrophilic polyurethane film having at least one surface coated with an organic polymer having pendant perfluoroalkylalkyl or perfluoroalkyl groups as side chains. The organic polymer imparts oleophobicity and hydrophobicity to the polyurethane film. The films have good water vapor transmission rate.		

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## WATER AND OIL REPELLENT POLYURETHANE FILM

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### FIELD OF THE INVENTION

This invention relates to water and oil repellent, polyurethane continuous films with good water vapor transmission rate (MVTR).

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### BACKGROUND OF THE INVENTION

There are two state-of-the-art methods to obtain a film that is water-proof but water vapor permeable. Method 1 employs hydrophobic polymeric membranes with microporous structures which allow only molecules in the vapor phase to pass through. A representative of this class of membranes or films is expanded porous polytetrafluoroethylene (ePTFE) which is described in U.S. Patent No. 3,953,566. Method 2 is to make a nonporous continuous hydrophilic polymeric film which is waterproof. The hydrophilicity of these films allows water molecules to pass through. It is obvious that the water vapor transmission mechanism is totally different for these two types of films. In Method 1 water vapor passes through the micropores but liquid water is prevented from passing through because of the hydrophobic nature of the polymer. In contrast in Method 2 there are no pores in the polymer, but water vapor can pass through because the polymer structure is such that it is amenable to molecular transfer of individual water vapor molecules.

Hydrophilic polyurethanes, i.e., polyurethanes with hydrophilic soft segments such as polyethylene oxide, are common continuous hydrophilic polymers used to make waterproof, water vapor permeable films, laminates thereof and continuous coatings thereof on textiles. These polymer films are disclosed in U.S. Patent No. 4,273,911, U.S. Patent No. 3,164,565, U.S. Patent No. 3,901,852, U.S. Patent No. 4,367,327, U. S. Patent No. 4,532,316, and U.S. Patent No. 4,686,137.

Due to the affinity of polyurethane for many solvents, oils and other organic liquids, polyurethane films have limited applications. They either swell or are dissolved upon contacting with solvents, oils and other liquids including water for hydrophilic polyurethane films. This property precludes their use or become a disadvantage in applications involving contacting with liquids that

swell or dissolve the film. It would be advantageous, and it is a purpose of this invention to provide a hydrophilic polyurethane, i.e., one that transports water vapor molecules, but which also has enhanced resistance to oil and water.

U.S. Patent No. 3,879,493 discloses a water vapor permeable polymeric composition comprising a homogeneous blend of a hydrophilic thermoplastic polymer with a hydrophobic polymer, mainly polyurethane. This has some enhanced polymer properties but does not have good water and oil repellence, or solvent resistance.

U. S. Patent No. 5,447,783 discloses a multicomponent film having three layers. The outer layers comprise a continuous layer of a hydrophobic copolyetherester elastomer. The inner middle layer is a continuous layer of a hydrophilic copolyetherester elastomer. U. S. Patent No. 4,769,273 disclosed a bicomponent film with a hydrophilic copolyester elastomeric layer and a hydrophobic copolyester elastomeric layer. These films are not adequate as water, oil and solvent repellents.

An article by H. Zhou *et al* (J. of East China Inst. Of Textile Sci. and Tech., English Edition, 1984, 1, No. 1, April, page 69) describes the production of waterproof, vapor-permeable coatings (for fabrics) by blending hydrophobic and lipophobic polymers. The coating films are not adequate as water, oil and solvent repellents.

Japanese Patent JP 62,103,134 discloses a waterproof, water vapor permeable composite by impregnating a hydrophobic polymer with cellulosic fiber, paper or non-woven fabrics. The hydrophobic polymers can be acrylic emulsions, synthetic rubber latex, polyurethane emulsion or vinylidenechloride latex.

There is a need for a waterproof, water and oil repellent, solvent resistant and water vapor permeable film of a hydrophilic polyurethane.

### **SUMMARY OF THE INVENTION**

As pointed out above, it is a purpose of this invention to provide a hydrophilic polyurethane with enhanced oil and water repellence.

More specifically, this invention is directed to the use of organic polymers containing perfluoroalkyl alkyl pendant side chain or side chains terminated with perfluoroalkyl alkyl groups as coatings on hydrophilic polyurethane substrate films. The organic polymer imparts water and oil repellence, while the hydrophilic polyurethane film remains hydrophilic and provides good moisture vapor transmission rates (MVTR).

By "hydrophilic" is meant that the polymer has an affinity for water and will allow water molecules to pass through.

By "pendant" is meant that the side chains depend from recurring backbone units of the polymer.

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### DETAILED DESCRIPTION OF THE INVENTION

#### Organic Polymers Containing Perfluoroalkyl Groups:

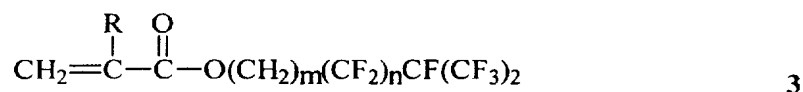
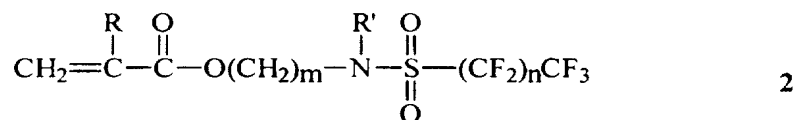
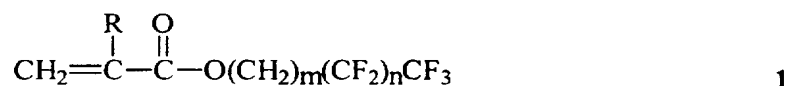
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The following polymers are examples of the polymers of this class.

(1) Polymers made from perfluoroalkyl acrylates and methacrylates:

Some monomers of this class of polymers are shown as in 1 - 3 below, where R = H or CH<sub>3</sub>; R' = H or lower alkyl such as methyl, ethyl, butyl; m is an integer from 1 to 15 and n is an integer from 3 to 17.

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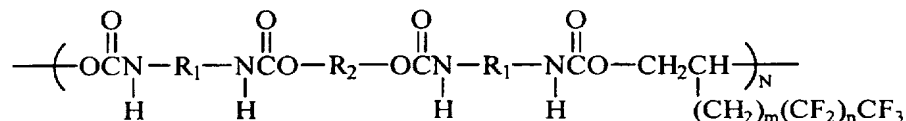
(2) Polyurethanes containing perfluoroalkyl groups:

These polymers contain urethane and/or urea groups and have pendant perfluoroalkyl groups or perfluoroalkyl group terminated side chains. This class of materials are particularly important because of their urethane nature which offers good adhesion with the polyurethane substrate film surface through strong interface interaction including hydrogen bonding and compatibility. The urethane and/or urea linkages can be either incorporated in main chain backbone or in pendant side chains. In other words, they can either be polyurethanes and/or ureas having pendant side chains terminated with perfluoroalkyl groups or any polymers having pendant side chains containing urethane and/or urea linkages as well as perfluoroalkyl groups as the terminate group. Some examples of this class of polymers are shown as below.

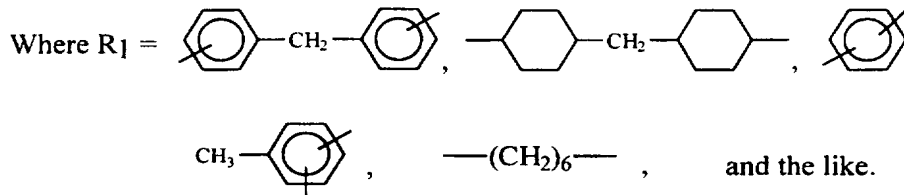
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(a) Polymers of the formula:

-4-



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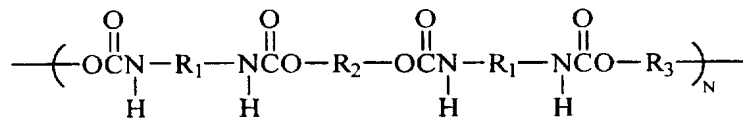


$\text{R}_2 =$  polyethers such as poly(ethylene oxide),  
 poly(tetramethylene oxide), polyesters such as  
 polycaprolactone, poly(hexamethylene adipate), alkyls  
 such as  $(\text{CH}_2)_{2-14}$  and the like.

$m$  is an integer from 1 to 15 and  $n$  is an integer from 3 to 17.

$N$  denotes number of repeating units of the polymer.

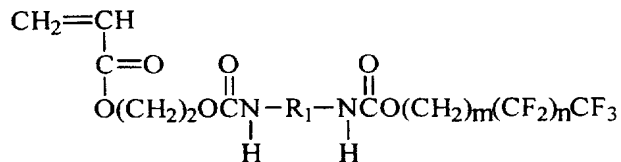
(b) Polymers of the formula:



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where  $\text{R}_1$ ,  $\text{R}_2$ ,  $N$ ,  $m$  and  $n$  are the same as those in 4.  $\text{R}_3$   
 is a linkage introduced from Poly-Fox Polyols which is a  
 polyether backbone with perfluoroalkyl pendant groups.

(c) Homopolymer of the monomer:



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- (d) Copolymers made from the monomer used in 6 and other copolymerizable monomers such as methyl (meth)acrylate, (methyl) butyl meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl acrylate, styrene, vinyl acetate, vinyl chloride, and the like.

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- (3) Other polymers that contain perfluoroalkyl side chain groups:

Other polymers that contain perfluoroalkyl group or perfluoroalkylalkyl can be used as coating materials. Such polymers include perfluorinated polyesters, polyamides, polyimides and vinyl polymers.

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#### Hydrophilic Polyurethane Films:

The hydrophilic polyurethane films used in this invention can be any type of polyurethanes having hydrophilic soft segments which have water vapor transmission properties. Films made from polyurethanes derived from polyethylene glycol diol and any type of diisocyanates and chain extender are particularly preferred. A specific example is the polyurethane made from polyethylene glycol diol, methylenedi-p-phenylene diisocyanate and a chain extender such as butanediol. The films can be made by extrusion or casting and range from 0.5 mil to 5.0 mil in thickness.

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#### Coating Processes:

Various types of coating processes can be used. Coating can be done by spray coating or dip-in coating or the like. Coating thickness is controlled by the method and by solid content (concentration) in the coating solution. Any other conventional coating methods may also be used.

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For solution coating, the guidelines for solvent selection are (1) the coating material must be able to be dissolved in the solvent, (2) the solvent should not dissolve the polyurethane film (3) the solvent can be removed below the temperature at which the polyurethane film melts and (4) the polyurethane film can be wetted by the solvent for uniform coating. Many common solvents meet these requirements.

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Due to the fact that hydrophilic polyurethanes are water wettable, Coating by aqueous emulsion of the polymer provides the most economic procedure.

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Coating on Both Sides:

Coating may be on both sides through dip-in coating method. The two side coated film of the invention is totally water and oil repellent and resistant. It has oil repellence rating greater than #8 (AATCC standard testing method-118) and water contact angle ranging from  $112^{\circ}$  to  $118^{\circ}$ , depending on coating material and coating thickness. However, water vapor can still pass through the film in high rate.

Coating on One Side ----- Asymmetric Film:

Coating can be performed only on one side of the film through either spray or kiss coating methods. The one side coated film results in an asymmetric film. This type of film has unique properties which offer special applications. The asymmetric film has one side with extremely low surface free energy and the other side with extremely high surface free energy. The low surface free energy side is hydrophobic and oleophobic. It is water and oil repellent and resistant has oil rating greater than #8 (AATCC standard testing method-118) and water contact angles ranging from  $112^{\circ}$  to  $118^{\circ}$ , depending on coating material and coating thickness. The high surface free energy side is hydrophilic and oleophilic, the same as uncoated film. It can be wetted by water and oil readily. The asymmetric film will have a different water vapor transmission rate depending on which side is placed toward a vapor source. In one test, when the low surface free energy side was toward water, an MVTR was obtained slightly lower than the untreated film. When the high surface free energy side was toward water, an MVTR was obtained that was the same value as the untreated film.

These unique properties of the asymmetric film can provide some special applications. For example, the film can be used in places where selective MVTR is required. It can be used in lamination with the high surface free energy side having better adhesion to the substrate, while the low surface free energy side is water and oil repellent and resistant.

Without intending to limit the scope of the present invention, the apparatus and method of production of the present invention may be better understood by referring to the following examples:

The oil rating tests were done with AATCC standard test method 118. The water contact angle measurements were performed on Rame-Hart Goniometer Model A100. MVTR values were obtained with Dry Modified



Desiccant Method (MDM dry method). In the MDM dry method, the sample is exposed to approximately 90% relative humidity (no water contact) on one side while a desiccant on the opposite side draws vapor through the material. The transmission rate is expressed in grams weight gain of the desiccant per square meter of material exposed to the desiccant per 24 hours ( $\text{g/m}^2 \cdot 24\text{hrs}$ ).

**Example 1:**

Milease F-95 emulsion, a perfluoroalkyl acrylate emulsion (50 ml), from Asahi Glass Co., Japan was mixed with 150 ml of water at room temperature to make a diluted emulsion. A polyethylene glycol diol and methylenedi-p-phenylene diisocyanate based hydrophilic polyurethane film of 1.0 mil thickness was treated on both sides with the diluted emulsion by means of a sprayer. The treated film was air dried to dryness and then heated in an oven at  $100^\circ\text{C}$  for 10 minutes.

Tested with #8 oil. The oil rolled off from the surface, indicating that it has an oil rating #8 or above. Water contact angle was  $112^\circ$ . MVTR was  $2,170 (\text{g/m}^2 \cdot 24\text{hrs})$ .

**Example 2:**

The same polyurethane film as that used in Example 1 was treated with the same diluted emulsion as that in Example 1 on one side of the film by spraying the emulsion on one side. The treated film was first air dried to dryness and then oven dried at  $100^\circ\text{C}$  for 10 minutes.

Test results from the treated side: Tested with #8 oil, the oil rolled off from the surface, indicating that it has oil rating #8 or above. Water contact angle was  $113^\circ$ . MVTR (measured by facing the treated side toward water) was  $1,591 (\text{g/m}^2 \cdot 24\text{hrs})$ .

Test results from the untreated side: Tested with #1 oil, the oil was absorbed into the film immediately, indicating that it has an oil rating less than #1. Water was also absorbed into the film immediately. MVTR (measured by facing the untreated side toward water) is  $4,071 (\text{g/m}^2 \cdot 24\text{hrs})$ .

**Example 3:**

A further diluted emulsion was prepared by adding 350 ml of water into 50 ml of the diluted emulsion from Example 1. The same film as in Example 1

was treated on both sides with such further diluted emulsion. The treated film was first air dried to dryness and then oven dried at 100°C for 10 minutes.

Tested with #8 oil, the oil rolled off from the surface, indicating that it has an oil rating #8 or above. Water contact angle was 116°. MVTR was 5,150 (g/m<sup>2</sup>.24hrs).

#### Example 4:

The same film as that used in Example 1 was treated on one side of the film with the same further diluted emulsion as that in Example 3 by spraying the emulsion on one side. The treated film was first air dried to dryness and then oven dried at 100°C for 10 minutes.

Test results from the treated side: Tested with #8 oil, the oil rolled off from the surface, indicating that it has an oil rating #8 or above. Water contact angle was 118°. MVTR (measured by facing the treated side toward water) was 3,472 (g/m<sup>2</sup>.24hrs).

Test results from the untreated side: Tested with #1 oil and also with water, both the oil and water were absorbed into the film immediately, indicating that it is water wettable and has an oil rating less than #1. MVTR (measured by facing the untreated side toward water) was 11,254 (g/m<sup>2</sup>.24hrs).

#### Example 5:

A polyethylene glycol diol and methylenedi-p-phenylene diisocyanate based hydrophilic polyurethane film of 2.0 mil thickness was treated on one side of the film with the same further diluted emulsion as that in Example 3 by spraying the emulsion on one side. The treated film was first air dried to dryness and then oven dried at 100°C for 10 minutes.

Test results from the treated side: Tested with #8 oil, the oil rolled off from the surface, indicating that it has an oil rating #8 or above. Water contact angle was 117°. MVTR (measured by facing the treated side toward water) was 4,253 (g/m<sup>2</sup>.24hrs).

Test results from the untreated side: Tested with #1 oil and also with water, both the oil and water were absorbed into the film immediately, indicating that it is water wettable and has an oil rating less than #1. MVTR (measured by facing the untreated side toward water) is 7,291 (g/m<sup>2</sup>.24hrs).

**Example 6:**

A solution was prepared by dissolving 1.5 grams of a copolymer containing units of perfluoroalkyl methacrylate in 100 ml of 1,3-trifluoromethyl benzene by warming. The same film as that used in Example 1 was treated with the solution on both sides by spraying. The treated film was first air dried to dryness and then oven dried at 100°C for 10 minutes.

Tested with #8 oil, the oil rolled off from the surface, indicating that it has an oil rating #8 or above. Water contact angle was 115°. MVTR was 7,493 (g/m<sup>2</sup>.24hrs).

**Example 7:**

The same film as that used in Example 1 was treated on one side of the film with the same solution as that in Example 6 by spraying the solution on one side. The treated film was air dried to dryness and then oven dried at 100°C for 10 minutes.

Test results from the treated side: Tested with #8 oil, the oil rolled off from the surface, indicating that it has an oil rating #8 or above. Water contact angle was 118°. MVTR (measured by facing the treated side toward water) was 6,885 (g/m<sup>2</sup>.24hrs).

Test results from the untreated side: Tested with #1 oil and also water, both the oil and water were absorbed into the film immediately, indicating that it is water wettable and has oil rating less than #1. MVTR (measured by facing the untreated side toward water) was 8,795 (g/m<sup>2</sup>.24hrs).

**Example 8:**

A diluted solution was prepared by adding 50 ml of 1,3-trifluoromethyl benzene to 25 ml of the solution from Example 6. The same film as that in Example 1 was treated with the diluted solution on both sides by spraying. The treated film was air dried to dryness and then oven dried at 100°C for 10 minutes.

Tested with #8 oil, the oil rolled off from the surface, indicating that it has an oil rating #8 or above. Water contact angle was 117°. MVTR was 7,840 (g/m<sup>2</sup>.24hrs).

**Example 9:**

The same film as that used in Example 1 was treated with the same diluted solution as that in Example 8 on one side of the film by spraying the solution on one side. The treated film was air dried to dryness and then oven dried at 100°C for 10 minutes.

Test results from the treated side: Tested with #8 oil, the oil rolled off from the surface, indicating that it has oil rating #8 or above. Water contact angle was 117°. MVTR (measured by facing the treated side toward water) was 8,043 (g/m<sup>2</sup>.24hrs).

Test results from the untreated side: Tested with #1 oil and also water, both the oil and water were absorbed into the film immediately, indicating that it is water wettable and has an oil rating less than #1. MVTR (measured by facing the untreated side toward water) was 13,163 (g/m<sup>2</sup>.24hrs).

**Example 10:**

The same film as that used in Example 5 was treated on both sides with the same diluted solution as that in Example 8 by spraying. The treated film was first air dried to dryness and then oven dried at 100°C for 10 minutes.

Tested with #8 oil, the oil rolled off from the surface, indicating that it has an oil rating #8 or above. Water contact angle was 118°. MVTR was 5,526 (g/m<sup>2</sup>.24hrs).

**Example 11:**

The same film as that used in Example 5 was treated on one side of the film with the same solution as that in Example 8 by spraying the solution on one side. The treated film was air dried to dryness and then oven dried at 100°C for 10 minutes.

Test results from the treated side: Tested with #8 oil, the oil rolled off from the surface, indicating that it has an oil rating #8 or above. Water contact angle was 117°. MVTR (measured by facing the treated side toward water) was 5,494 (g/m<sup>2</sup>.24hrs).

Test results from the untreated side: Tested with #1 oil and also water, both the oil and water were absorbed into the film immediately, indicating that it is water wettable and has an oil rating less than #1. MVTR (measured by facing the untreated side toward water) was 7,667 (g/m<sup>2</sup>.24hrs).

**Example 12:**

5 Milease F-95 emulsion, a perfluoroalkyl acrylate aqueous emulsion from (20 ml) Asahi Glass Company, Japan was mixed with 80 ml of water at room temperature to make a diluted emulsion. The same film as that used in Example 1 was treated with the emulsion on one side of the film by spraying the emulsion on one side. The treated film was air dried to dryness and then oven dried at 100°C for 10 minutes.

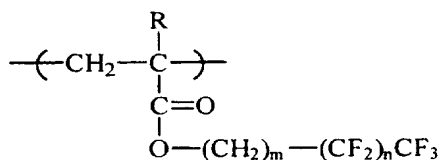
10 Test results from the treated side: Tested with #8 oil, the oil rolled off from the surface, indicating that it has an oil rating #8 or above. It was water repellent. MVTR (measured by facing the treated side toward water) was 2,112 (g/m<sup>2</sup>.24hrs).

15 Test results from the untreated side: Tested with #1 oil and also water, both the oil and water were absorbed into the film immediately, indicating that it is water wettable and has an oil rating less than #1. MVTR (measured by facing the untreated side toward water) was 5,092 (g/m<sup>2</sup>.24hrs).

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**WE CLAIM:**

1. A hydrophilic polyurethane film having at least one surface coated with an organic polymer having pendant perfluoroalkylalkyl or perfluoroalkyl groups as side chains.
2. The polyurethane film of Claim 1 wherein the organic polymer has pendant perfluoroalkylalkyl groups as side chains.
3. The polyurethane film of Claim 2 wherein the organic polymer is a perfluoroalkylalkyl acrylate or methacrylate.
4. The polyurethane film of Claim 3 or 4 wherein the perfluoroalkylalkyl groups have the formula
 
$$\text{CF}_3-(\text{CF}_2)_n-(\text{CH}_2)_2$$
 wherein n is an integer of 3-17.
5. The polyurethane film of Claim 1 wherein the organic polymer contains urethane or urea linkages.
6. The polyurethane film of Claim 1 or 5 wherein the organic polymer has recurring structural units of the formula



wherein R is H or -CH<sub>3</sub>, m is an integer of 1-15 and n is an integer of 3-17.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/00512

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08J7/04 C09D133/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08J C09D C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Week 9117 Derwent Publications Ltd., London, GB; AN 91-121691 XP002030976 &amp; JP 03 061 041 A (DYNIC CORP) , 15 March 1991 see abstract</p>	1-4,6
A	<p>--- EP 0 339 880 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 2 November 1989 see claims 1,2,7 see page 5, line 3-7</p>	1
A	<p>--- GB 1 262 526 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 2 February 1972 see claims 1-7 see page 3, line 1-23 ---</p>	1-3

-/-

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

21 May 1997

Date of mailing of the international search report

- 6. 06. 97

Name and mailing address of the ISA

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In tional Application No  
PCT/US 97/00512

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 331 307 A (E.I. DU PONT DE NEMOURS AND COMPANY) 6 September 1989 see claim 1 see example 9</p> <p>-----</p>	1,5



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